I. Physical Properties Studies

A. Polymer Degradation Mechanisms

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1. Kinetic Studies of Chain Scission of POPG–TDI and a Block (POEG–POP)–TDI Polymer

Degradation of polymers is being studied to provide a chemical basis for the development of nondestructive test methods applicable to solid propellants which may undergo chemical changes before use. Thermal degradation of uncrosslinked polyoxypropylene glycol–toluene diisocyanate polymer (POPG–TDI) and related polymers are being investigated to determine the mechanism of bond scission.

Although chain scission of POPG–TDI at 200°C has been shown to take place predominately at the urethane bonds by a random mechanism (*SPS 37-17*, Vol. IV) it is not expected that all the urethane bonds will break at the same rate. The 2- or 4-isocyanate groups form bonds with primary or secondary hydroxyls of different stability and these four possible urethane types will degrade at different rates. Furthermore, weak links other than urethanes can be postulated, for example, peroxides in the polyether, or dimerized isocyanates. In an attempt to determine whether the initial rate of bond scission would be decreased by a larger concentration of primary hydroxyl groups in the starting polyoxyalkylene glycol, a block (polyoxyethylene glycol–polyoxypropylene)–toluene diisocyanate (POEG–POP)–TDI polymer was prepared for degradation. The POPG was reacted with sodium and then treated with ethylene oxide at 130 to 140°C until 3.76 mole of epoxide per equivalent of hydroxyl was reacted. After thorough washing and drying the POEG–POP was reacted with TDI. A similar polyurethane was prepared from unmodified POPG and both samples were degraded at 200°C under helium. The degradation was followed by withdrawing samples for intrinsic viscosity $[\eta]$, and infrared measurements. Although the infrared studies indicated decreasing urethane hydrogen and increasing hydroxyl at large extents of degradation, because of band overlap and sample and cell variability, quantitative results were not obtained. From η the weight average molecular weight M_w was estimated by means of the equation (Ref. 2)

$$[\eta] = 4.13 \times 10^{-4} M_w^{0.64}$$

It has been shown (*SPS 37-16*, Vol. IV) that the ratio of the weight average molecular weight M_w, to number

average molecular weight M_n for most probable distributions is given by

$$M_w/M_n = 2/(1 + M_u/M_w)$$

or

$$M_n = (M_w + M_u)/2$$

Therefore, M_n was calculated from M_w and an assumed value of the unit molecular weight $M_u = 1100$, the average spacing of urethane links. The value of M_u was also used to calculate the number degree of polymerization X_n. In addition, the average number of cuts per molecule S, and the fraction of urethane links broken F, were calculated from

$$S = (X_{n(0)}/X_{n(t)}) - 1$$

and

$$F = S/(X_{n(0)} - 1)$$

in which $X_{n(0)}$ and $X_{n(t)}$ are the number average degrees of polymerization at time zero and time t, respectively. For a system undergoing strictly random degradation, the integrated rate equation is

$$-\log\left(\frac{X_{n(t)} - 1}{X_{n(t)}}\right) = -\log\left(\frac{X_{n(0)} - 1}{X_{n(0)}}\right) + kt$$

For such a process a plot of $-\log [(X_{n(t)}-1)/X_{n(t)}]$ versus time t, should give a straight line with a slope k and an intercept of $-\log [(X_{n(0)}-1)/X_{n(0)}]$ (Ref. 3).

The results for POPG–TDI and the POEG–POP–TDI polymers are given in Table 1 and Fig. 1, and the

$$-\log [(X_{n(t)}-1)/X_{n(t)}]$$

versus t plot in Fig. 2. It is apparent from the decrease in $[\eta]$ and the values of S and F that the initial rate of degradation is much less for the block polymer. Fig. 2

Table 1. Thermal degradation of POPG–TDI and a block (POEG–POP)–TDI polymer at 200°C under helium

Polymer	Time, min	Intrinsic viscosity,[a] $[\eta]$, dl/g	Weight average molecular wt,[b] $M_w \times 10^{-3}$	Number average molecular wt,[c] $M_n \times 10^{-3}$	Number average chain length,[d] X_n	$-\log \frac{X_n - 1}{X_n}$	Number of cuts,[e] S	Extent of degradation,[f] F
POPG–TDI	0	0.336	35.5	18.29	16.63	0.02664	0.0	0.0
	15	0.243	21.4	11.24	10.22	0.04455	0.6275	0.04015
	75	0.202	16.0	8.55	7.775	0.05973	1.140	0.07295
	135	0.195	15.0	8.055	7.322	0.06374	1.270	0.08125
	195	0.176	12.9	7.000	6.364	0.07417	1.613	0.1032
	255	0.166	11.7	6.400	5.816	0.08176	1.860	0.1190
	315	0.160	11.0	6.050	5.500	0.08725	2.025	0.1296
	375	0.153	10.4	5.750	5.227	0.09232	2.181	0.1395
	460	0.150	10.0	5.550	5.044	0.09583	2.297	0.1469
	1635	0.118	6.95	4.023	3.657	0.13847	3.548	0.2271
	3165	0.102	5.45	3.274	2.977	0.17751	4.585	0.2933
(POEG–POP)–TDI	0	0.478	62.0	31.55	28.69	0.01525	0.0	0.0
	15	0.450	56.0	28.53	25.95	0.01705	0.1060	0.03829
	75	0.409	49.0	25.04	22.77	0.01932	0.2590	0.009360
	135	0.371	41.8	21.45	19.50	0.02273	0.4710	0.01701
	255	0.229	19.5	10.30	9.370	0.04905	2.062	0.07450
	315	0.206	16.8	8.96	8.145	0.05690	2.522	0.09110
	375	0.190	14.6	7.850	7.138	0.06550	3.020	0.1091
	460	0.180	13.3	7.200	6.545	0.07186	3.383	0.1222
	1635	0.138	8.8	4.950	4.500	0.10902	5.378	0.1943
	3195	0.121	7.2	4.147	3.770	0.13401	6.610	0.2388

[a] Determined in benzene solutions at 25°C and calculated from $\eta_{sp}/c = [\eta] + k'[\eta]^2 c$, using $k' = 0.39$ (Ref. 1).
[b] From $[\eta] = 0.413 \times 10^{-4} M_w^{0.64}$.
[c] From $M_n = (M_w + M_u)/2$, assuming $M_u = 1100$.
[d] From $X_n = M_n/M_u$, assuming $M_u = 1100$.
[e] From $S = X_{n(0)}/X_{n(t)} - 1$.
[f] From $F = S/(X_{n(0)} - 1)$; F is the fraction of urethane bonds broken.

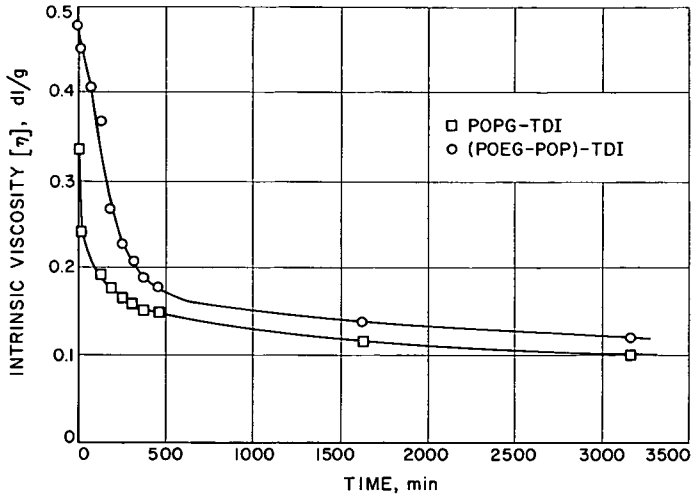

Fig. 1. Decrease of intrinsic viscosity on thermal degradation of POPG–TDI and block (POEG–POP)–TDI polymers at 200°C under helium

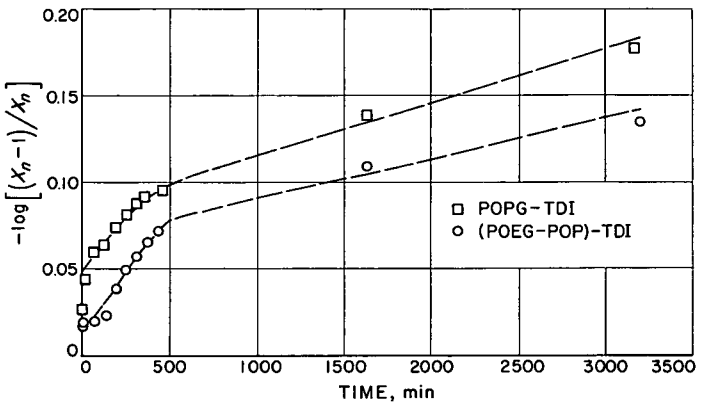

Fig. 2. Kinetic plot of thermal degradation of POPG–TDI and block (POEG–POP)–TDI polymers at 200°C under helium

shows that neither polymer exhibits strictly random degradation since the available cleavable bonds undergo scission at different decreasing rates as degradation proceeds. Extrapolation of the first straight line portion of the curve for POPG–TDI to zero time gives a molecular weight of 10,000, which represents the spacing of the very weak links. Since a similar extrapolation for (POEG–POP)–TDI gives the initial molecular weight, such weak links do not appear to be present in this polymer. The results indicate that the weak links involve terminal secondary hydroxyls on the POPG, presumably reacted with *ortho*-isocyanate groups. However, this must be regarded as a tentative conclusion based on a single experiment. One obvious objection that arises is that the weak bond spacing is too large if all the urethane bonds formed from secondary hydroxyl and *ortho*-isocyanate groups are involved, since such bonds are present in higher concentration than one per 5 POPG units. Since it is possible that a small contaminating precursor for weak link formation may have been removed from the POEG–PPG during block polymer preparation that was still present in the POPG control sample, further experiments will include parallel treatment of the POPG reacted with ethylene oxide and a control preparation omitting only the ethylene oxide addition. In addition, the degradation studies will be extended to lower temperatures in an attempt to determine the energy of activation for weak link scission in POPG–TDI polymer.

2. *The Huggins Constant k′ for POPG and Degraded POPG-TDI Polymers*

For benzene solutions of POPG–TDI at 25°C the Huggins Constant k' has been found to be ~0.39 for

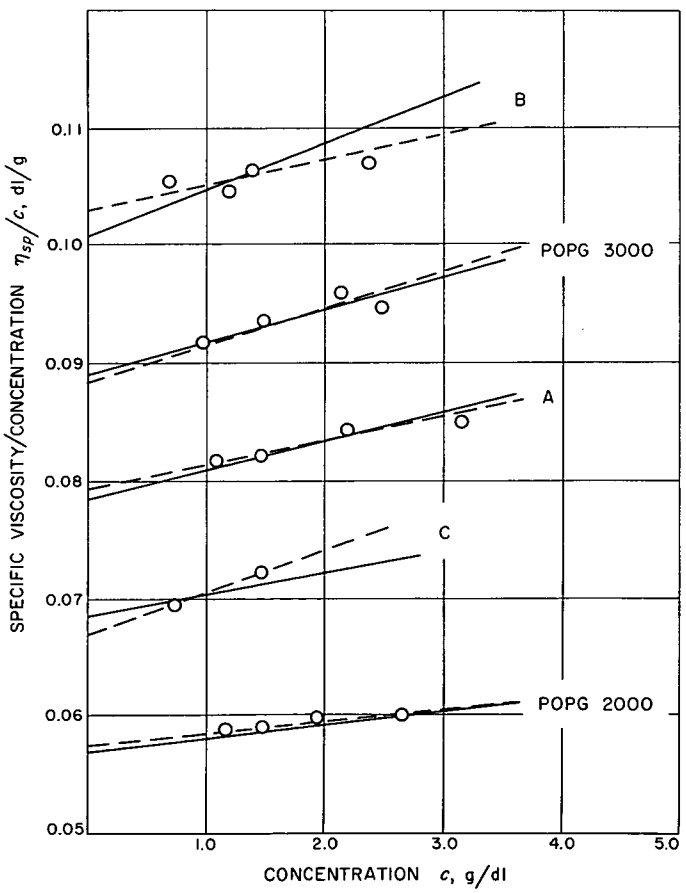

Fig. 3. Plots of η_{sp}/c versus c for POPG-2000, POPG-3000 and degraded POPG-TDI polymers A, B, and C

Table 2. Intrinsic viscosity measurements on POPG and degraded POPG-TDI polymers

Sample	Concentration c, g/dl	Specific viscosity η_{sp}	η_{sp}/c	Intrinsic viscosity[a] $[\eta]$, dl/g	Average intrinsic viscosity[a] $[\eta]$, dl/g	Intrinsic viscosity[b] $[\eta]$, dl/g	Constant[c] k' calculated
POPG-2000	2.65	0.158	0.0597	0.056	0.0570	0.0576	0.38
	1.93	0.115	0.0597	0.057			
	1.44	0.0852	0.0590	0.057			
	1.16	0.0682	0.0590	0.058			
POPG-3000	2.49	0.235	0.0946	0.087	0.0885	0.0883	0.43
	2.13	0.205	0.0959	0.089			
	1.49	0.140	0.0936	0.089			
	0.996	0.0914	0.0917	0.089			
A	3.14	0.266	0.0850	0.078	0.0785	0.0793	0.31
	2.20	0.185	0.0843	0.079			
	1.46	0.120	0.0821	0.078			
	1.098	0.0897	0.0817	0.079			
B	2.39	0.257	0.1072	0.098	0.1007	0.1027	0.21
	1.40	0.149	0.1064	0.101			
	1.20	0.126	0.1045	0.101			
	0.699	0.0738	0.1056	0.103			
C	1.46	0.105	0.0722	0.069	0.0685	0.0670	0.79
	0.728	0.0506	0.0695	0.068			

[a] These intrinsic viscosities were obtained by calculation assuming $k' = 0.39$ for each concentration.

[b] These intrinsic viscosities were obtained by extrapolation to infinite dilution from the plot of η_{sp}/c versus c.

[c] These values of k' were calculated from the equation $\eta_{sp}/c = [\eta] + k'[\eta]^2 c$ from the plot of η_{sp}/c versus c.

intrinsic viscosities from 0.1 to 0.6 (Ref. 1). In the present work this value has been assumed to be valid for POPG and highly degraded POPG–TDI polymers. Ordinarily η_{sp} is determined for two concentrations and $[\eta]$ calculated from $\eta_{sp}/c = [\eta] + 0.39[\eta]^2 c$. Since the two values of $[\eta]$ generally agree within 0.002 dl/g, use of $k' = 0.39$ is apparently justified. In an effort to determine an experimental value for k' and more adequately assess the possible errors resulting from the assumption that $k' = 0.39$ for POPG and degraded POPG–TDI polymers, some viscosity data at different concentrations have been obtained and are shown in Table 2 and Fig. 3. The solid lines in Fig. 3 have slopes such that $k' = 0.39$; the dashed lines were previously established from the experimental points. Although values of k' from the latter deviate widely from 0.39, the solid lines fit the data within the limits of error and the intrinsic viscosities obtained from either line agree within 0.002 dl/g. Therefore, use of $k' = 0.39$ for polymers of this type should not result in large errors in $[\eta]$. For a unique determination of the true values of k', more accurate data are required. Greater precision could be obtained by increasing the concentration to give higher relative viscosities; however, the results of Fig. 3 indicate that the η_{sp}/c versus c plots may not be linear at concentrations much greater ~2 g/dl.

B. A Study of the Ultimate Properties of Amorphous Gum Vulcanizates

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1. Introduction

An understanding of the molecular mechanisms which control the ultimate properties of elastomeric materials would be of considerable utility from the standpoint of both theoretical and practical applications. A working theory of the ultimate property behavior of vulcanizates would constitute a long step in contributing a basis for the design of polymeric materials to desired specifications; in addition, once the molecular basis for ultimate property behavior in amorphous gum vulcanizates is understood, then there will be sound basis for understanding the like behavior of filled systems. One pre-